



# PATENT SPECIFICATION

NO DRAWINGS

83  
921682

Date of Application and filing Complete Specification: Aug. 11, 1960.

No. 27788/60.

Application made in Switzerland (No. 76959) on Aug. 14, 1959.

Complete Specification Published: March 20, 1963.

GT. BRIT.

DIV.

Index at acceptance:—Classes 2(3), C1Q(2:5:6B1:7A:8A:8B:8C:9A:9F1:9G:9K:11G:11J); 15(2), P3(B:F2:G1:G2:G5); 81(1), B1(F:G:H:N:Q:S:T), E1A(3A4:3B3:4A2:4A3:4A4:11:12:15), E1C(3A4:3B3:4A2:4A3:4A4:11:12:15) L1; and 91, D2(E:F:G:H:K:L:N:R:S), D3, DS2(E:F:G:H:K:L:N:R:S).

International Classification:—C07c. A61k, I. C11d. D06m.

## COMPLETE SPECIFICATION

### New Diphenyl Urea Derivatives, processes for their production and Compositions containing same

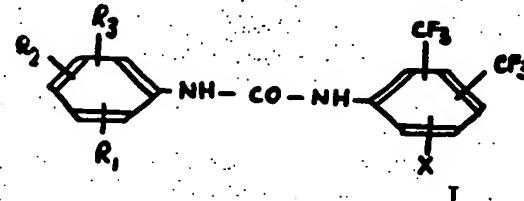
We, J. R. GEIGY A.-G. a body corporate organised according to the laws of Switzerland, of 215, Schwarzwaldallee, Basle, Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention concerns a process for the production of new insecticidal and bactericidal derivatives of diphenyl urea which have an affinity to keratin fibres in aqueous dispersion and which protect the treated keratin material from attack and injury by larvae of microlepidopters (such as moths) and certain species of beetle (such as fur and carpet beetles). The invention also concerns the diphenyl urea derivatives obtained by the production process as well as the pest control agents containing these new compounds as active substances and the use of the new compounds for pest control, in particular for the protection of keratin material from injury by insects and also the keratin material protected in this way from injurious insects. In addition, the invention also concerns disinfectants and disinfectant cleansing agents, in particular textile washing agents and toilet soaps, which contain the new active substances as well as the use of these agents for the disinfection or simultaneous cleansing and disinfection of objects of all types, in particular also of fabrics containing cellulose.

It is known that halogenated diphenyl ureas have antibacterial and insecticidal properties which are particularly marked if there is a  $CF_3$  group in the molecule.

It has now surprisingly been found that substituted diphenyl urea derivatives having two  $CF_3$  groups in one benzene nucleus, of the general formula

[Price 4s. 6d.]



wherein  $R_1$  represents hydrogen, a halogen atom, the trifluoromethyl group or the nitro group.

$R_2$  represents hydrogen, a halogen atom, the trifluoromethyl group or an alkyl or alkoxy radical having from 1 to 5 carbon atoms.

$R_3$  represents hydrogen, a halogen atom or a phenoxy or phenylmercapto radical possibly substituted by one or more chlorine atoms or alkyl groups having from 1 to 5 carbon atoms, and

X represents hydrogen, a halogen atom or an alkoxy group having from 1 to 5 carbon atoms,

have considerably better insecticidal activity, in particular against insects, in all stages of their development, which are injurious to keratin material such as moth larvae, fur and carpet beetle larvae and, in addition, are suitable, because of their better bactericidal activity, as disinfectant and antibacterial active ingredients for the production of disinfectants and also of disinfectant washing and cleansing agents. In the general formula I, the two  $CF_3$  groups are advantageously in the meta position with regard to each other, in particular in the 3- and 5-positions of the benzene nucleus.

The new diphenyl urea derivatives of the general formula I are produced according to

45

50

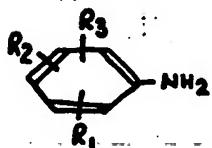
55

60

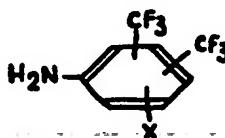
65

70

the invention, by reacting by known methods, possibly in steps, one mol of a reactive derivative of carbonic acid with one mol of each of two aminobenzene compounds of the 5 general formulae



II



III

wherein R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and X have the meanings given above.

10 Diphenyl urea derivatives of the general formula I which are particularly insecticidally active are those in which the two CF<sub>3</sub> groups are in the 3- and 5-positions of the first phenyl radical and in which the other phenyl radical is substituted either by two chlorine atoms in 15 the 3- and 4-positions to the carbamide bridge or by one CF<sub>3</sub> group in the 3-position; in the latter case, the 4-position of the phenyl radical can be further substituted by a chlorine atom.

20 Principally chlorine and bromine are employed as halogen substituents of the phenyl radicals, but the corresponding fluorine and iodine compounds are also active.

25 Examples of suitable substituted starting aminobenzene compounds of the general formula II are, besides aniline: 3,5 - bis - (trifluoromethyl) - aniline, 3 - trifluoromethyl - 4 - chloraniline, 3 - trifluoromethyl - 6 - chloraniline, 3,5 - dichlor-, 3,4,5 - tri-30 chlor-, 2,4,5 - trichlor-, 2 - methoxy - 4,5 - dichlor - aniline, 3 - trifluoromethyl - 4 - ethoxy aniline, 2 - trifluoromethyl - 4,5 - dichloraniline, 4 - nitro-aniline, 4 - chloroaniline, 3,4 - dichloro- aniline, 2 - chloro - 5 - trifluoromethyl - aniline, 3 - trifluoromethyl aniline, 2,4 - dichloroaniline, 3 - chloro - 4 - bromaniline, 2,4 - dibromaniline, 3 - chloro - 4 - trifluoromethyl aniline, 2,5 - dichloro - 4 - trifluoromethyl aniline and 2 - nitro - 4 - chloraniline; as starting materials of the general formula II containing phenoxy or phenylmercapto groups can be mentioned: 4 - phenoxy-, 3 - phenoxy-, 4 - (4<sup>1</sup> - chlorophenoxy)-, 2 - (4<sup>1</sup> - chlorophenoxy) - 5 - chloro-, 4 - (3<sup>1</sup>,4<sup>1</sup> - dichlorophenoxy)-, 4 - (2<sup>1</sup>,4<sup>1</sup> - dichlorophenoxy)-, 2 - (4<sup>1</sup> - chlorophenoxy) - 5 - trifluoromethyl-, 2 - (4<sup>1</sup> - amylphenoxy) - 5 - chloro-, 2 - (4<sup>1</sup> - chlorophenoxy) - 5 - methyl-, 2 - (3<sup>1</sup>,4<sup>1</sup> - dichlorophenoxy) - 5 - methyl-, 4 - (4<sup>1</sup> - amylphenoxy)-, 4 - (4<sup>1</sup> - isobutylphenoxy)-, 2 - (4<sup>1</sup> - methylphenoxy) - 5 - methyl-, 2 - (3<sup>1</sup>,4<sup>1</sup> - dimethylphenoxy) - 5 - methyl-, 4 - (4<sup>1</sup> - chlorophenylmercapto)- and 4 - (4<sup>1</sup> - methylphenylmercapto)- aniline.

The preferred starting aminobenzene compound of the general formula III is 3,5 - bis - (trifluoromethyl) - aniline. As other starting materials of the general formula III can be mentioned: 3,5 - bis - (trifluoromethyl) - 4 - chloraniline and 2,4 - bis - (trifluoromethyl) - 6 - methoxy aniline.

As reactive derivatives of carbonic acid in the process according to the invention are used: the acid halides in particular phosgene, the acid esters in particular the phenol esters, the acid halide monoesters particularly the chlorocarbonic acid phenyl esters, the acid amides or imides particularly urea. Principally phosgene and the chlorocarbonic acid phenyl esters are used in the stepwise reaction for the production of unsymmetrically substituted diphenyl urea derivatives of the above formula I. For this purpose, these are reacted by methods known per se first with 1 mol of one of the two aminobenzene compounds of the formulae II or III used according to the invention to form the corresponding phenyl carbamic acid chlorides or phenol esters which are then reacted with 1 mol of the other aminobenzene compound to form the diphenyl urea derivative. If desired, the reaction products of 1 mol of phosgene with 1 mol of aminobenzene compound of the formula II or III can be converted, also by known methods, for example by heating in inert higher boiling organic solvents such as nitrobenzene or o-dichlorobenzene while splitting off hydrogen halide, into the phenyl isocyanates corresponding to the aminobenzene compounds listed above and then suitably chosen aminobenzene compounds of the formula III or II can be added to these compounds. Symmetrically substituted derivatives of diphenyl urea according to the invention, such as e.g. 3,5,3<sup>1</sup>,5<sup>1</sup> - tetra - (trifluoromethyl)-diphenyl urea, are produced advantageously by heating 2 mol of the bis-(trifluoromethyl) - aminobenzene compound with 1 mol of urea or phosgene, e.g. in aqueous solution, whereupon the diphenyl urea derivative separates direct in a pure form while ammonia or hydrochloric acid is split off.

The new insecticidal derivatives of diphenyl urea are white, well crystallised substances which have defined melting points. They are practically insoluble in water but dissolve well, particularly in the warm, in organic solvents such as, e.g. dialkyl ketones, chlorobenzene, nitrobenzene, ethylene glycol monoalkyl ethers and pyridine bases.

For use in an aqueous liquor, advantageously the finely milled powders of the active substance or its solution in an organic solvent which is miscible with water, are mixed with capillary active wetting and dispersing agents such as, e.g. with the formaldehyde condensation product of naphthalene sulphonic acid or with the polyalkylene glycol ethers of phenols

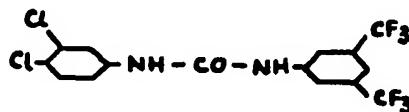
which contain a higher molecular aliphatic or alicyclic hydrocarbon radical as ring substituent. On stirring such preparations in aqueous treatment liquors, milky dispersions are obtained, from which the diphenyl urea derivatives according to the invention are fixed fast to washing, milling, light and dry cleaning onto keratin fibres, in particular wool, in the warm. Keratin fibres treated in this way with a content of at least 0.1 to 0.5% of active substance are durably protected from injury by larvae of microlepidopters and certain types of beetle.

Compared with the known, halogenated diphenyl ureas or those containing  $\text{CF}_3$  groups, the new compounds having two  $\text{CF}_3$  groups in the same benzene ring have the advantage of considerably greater activity, particularly against the injurious larvae of *Attagenus* and *Anthrenus* species.

The following examples illustrate the production process according to the invention. Parts are given therein as parts by weight and the temperatures are in degrees Centigrade.

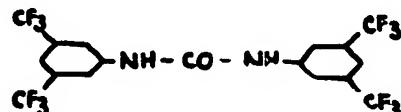
25

## EXAMPLE 1



229 Parts of 3,5 - bis - (trifluoromethyl) - aniline are added to a solution of 188 parts of 3,4 - dichlorophenyl isocyanate (produced by known methods from 3,4 - dichloraniline and phosgene, see, for example, W. Siefken, *Annalen der Chemie*, 562, 96-136, (1948)) in 1000 parts of nitrobenzene. The reaction mixture is heated for 3 hours at  $80^\circ$ . On cooling, the greater part of the diphenyl urea derivative precipitates. It is filtered off under suction and further purified by recrystallisation from methanol. The pure 3,5 - bis - (trifluoromethyl) - 3<sup>1</sup>,4<sup>1</sup> - dichloro - N,N<sup>1</sup> - diphenyl urea melts at 210-212°.

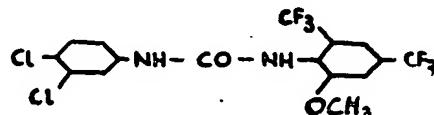
## EXAMPLE 2



229 Parts of 3,5 - bis - (trifluoromethyl) - aniline are dissolved in 800 parts of acetone. Phosgene is introduced into this solution at 35-40° and at the same time a solution of 190 parts of sodium acetate in 500 parts of

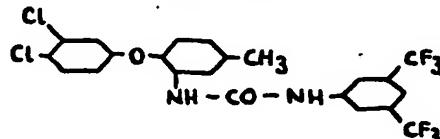
water is added dropwise. Phosgene is introduced until the solution just becomes weakly acid. The reaction mixture is then diluted with water and the precipitate which forms is filtered off under suction. After washing with water it is recrystallised from methanol. The melting point of the pure 3,5,3<sup>1</sup>,5<sup>1</sup> - tetra - (trifluoromethyl) - N,N<sup>1</sup> - diphenyl urea is 242-243°.

## EXAMPLE 3



259 Parts of 2 - methoxy - 4,6 - bis - (trifluoromethyl) - aniline are dissolved in 600 parts of chlorobenzene and 188 parts of 3,4 - dichlorophenyl isocyanate are added to this solution dropwise at  $60^\circ$ . The reaction mixture is kept for 4 hours at  $60-65^\circ$  and then cooled whereupon the greater part of the reaction product precipitates in crystalline form. It is filtered off under suction and, in the crude form, melts at 200-210°. The pure compound is obtained by recrystallising twice, first from chlorobenzene and then from isopropanol. It then melts at 220-222°.

## EXAMPLE 4



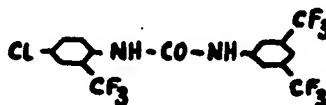
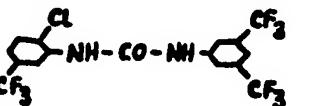
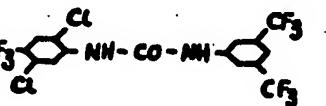
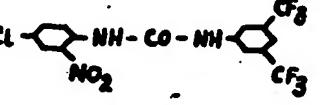
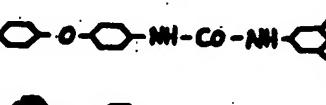
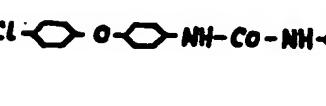
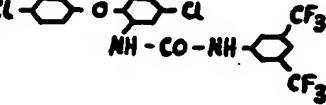
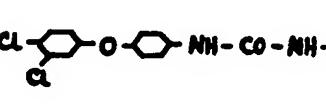
A solution of 252 parts of 3,5 - bis - (trifluoromethyl) - phenyl isocyanate in 2000 parts of chlorobenzene is added dropwise to a previously prepared solution of 278 parts of 2 - amino - 4 - methyl - 3<sup>1</sup>,4<sup>1</sup> - dichlorodiphenyl ether in 1000 parts of benzene. The mixture is heated for 6 hours at  $80-85^\circ$ . After cooling, the crude product is filtered off under suction and, after drying in vacuo, it melts at about 180°. The compound is purified by recrystallising twice from chlorobenzene and then melts at 190-192°.

The following compounds can be produced as described in the previous examples from carbonic acid derivatives, and corresponding starting materials of formula II or their isocyanates, and 3,5 - bis - (trifluoromethyl) - aniline; wool treated with these compounds is protected from injury by the larvae of moths, fur and carpet beetles.

	diphenyl urea derivative	M.P.
		164-166°
		212-214°
		318-321°
5		280-283°
		190-193°
		203-205°
		194-197°
		289-293°
10		212-213°
		183-184°
		172-173°

## diphenyl urea derivative

## M.P.

		202-203°
		208-210°
5		190-192°
		184-186°
		171-172°
		176-177°
		181-183°
10		196-198°
		198-199°

It was not to have been expected that the active substances used according to the invention would retain their antibacterial activity in the presence of capillary active substances, 5 in particular in the presence of the alkali metal soaps of higher fatty acids which are the most important components of washing agents. The active substances used also have good fastness to light so that they cause practically no 10 yellowing in soaps.

Apart from the active substances, the soaps or other washing and cleansing agents can contain the usual fillers such as alkali sulphates, 15 carbonates or phosphates as well as the other additives usual in cleansing agents.

The disinfectant cleansing agents according to the present invention can be put to the most various uses. For example, they can be used in human and veterinary hygiene for 20 cleansing and simultaneous protection against bacteria causing diseases either direct on the skin or via the mouth or causing perspiration odours. Examples of such infective bacteria are *Staphylococcus aureus*, *Escherichia coli*, 25 *Sarcina lutea* and *Sarcina alba*, and of those decomposing perspiration are *Proteus vulgaris*, *Bacillus mesentericus* and *Bacillus subtilis*. In such cases, the most usual cleansing agent components are soaps, but also, according to 30 the present invention, the antibacterial active ingredients defined above can also be combined with cosmetics such as ointments, creams or skin lotions which contain other capillary active substances, for example in the form of 35 dispersing agents.

Naturally, disinfectants can also be produced which, in addition to the active substances according to the present invention, contain other active ingredients which are 40 suitable for increasing or modifying the action.

Disinfectant cleansing agents according to the present invention can also be used, for example, for the cleansing of textiles or leather; the ready-for-use soaking, washing, cleansing 45 and rinsing liquors to which the antibacterial active ingredients have been added later, i.e. after dissolving the capillary active substances in water, also being washing and cleansing agents according to the present invention. Like 50 the use thereof, they also fall within the scope of the present invention. Also, the substituted diphenyl ureas of the general formula I can be combined with dry cleaning agents, i.e. dissolved in aliphatic or aromatic, possibly 55 chlorinated, hydrocarbons, most of which generally also contain capillary active wetting and cleansing agents which are soluble in oil.

Finally, the antibacterial cleansing agents according to the present invention can be used 60 also for the disinfection of other organic or inorganic objects. Thus, they are valuable, for example, for the antibacterial cleansing of apparatus and objects in hospitals such as surgical instruments, instrument tables, vessels, 65 and laboratory utensils, as well as of equip-

ment and vessels in food and fermentation industries.

Preferred active ingredients of general formula I are 3,5 - bis - (trifluoromethyl) - 3<sup>1</sup>,4<sup>1</sup> - dichloro - N,N<sup>1</sup> - diphenyl urea and 3,5 - bis - (trifluoromethyl) - 4<sup>1</sup> - chloro - N,N<sup>1</sup> - diphenyl urea.

The following examples illustrate the production of the disinfectants and disinfectant 70 cleansing agents according to the invention as well as the use of these agents. Parts are given therein as parts by weight and the temperatures are in degrees Centigrade.

#### EXAMPLE 6

75 Parts of coconut oil (saponification number 262) and 25 parts of castor oil (saponification number 175) are saponified at 115° with 120 parts of an about 15% sodium hydroxide solution. 3 Parts of 3,5 - bis - (trifluoromethyl) - 3<sup>1</sup>,4<sup>1</sup> - dichloro - N,N<sup>1</sup> - diphenyl urea or 3,5 - bis - (trifluoromethyl) - 4<sup>1</sup> - dichloro - N,N<sup>1</sup> - diphenyl urea are then added to the still liquid soap and the mixture is homogenised well. After salting out, the soap is poured into moulds and allowed to cool. 80 Pieces of household soap are obtained which, on being used for washing, are characterised by a good antibacterial action.

#### EXAMPLE 7

To produce an antibacterial toilet soap, 98 parts of soda soap filings are well mixed with 2 parts of 3,5 - bis - (trifluoromethyl) - 4<sup>1</sup> - chloro - N,N<sup>1</sup> - diphenyl urea. The mixture is then milled and pressed into the usual moulds.

#### EXAMPLE 8

A combination of 2 parts of 3,5 - bis - (trifluoromethyl) - 4<sup>1</sup> - chloro - N,N<sup>1</sup> - diphenyl urea with 25 parts of triethanolamine salt of n-dodecyl sulphuric acid, 1 part of n-dodecyl alcohol, 3 parts of triethanolamine sulphate, 1 part of lauric acid mono-glyceride and 68 parts of water can be used as a liquid 90 toilet soap and also as shampoo. It has a good antibacterial action.

#### EXAMPLE 9

5 Parts of 3,5,3<sup>1</sup> - tri - (trifluoromethyl) - 4<sup>1</sup> - chloro - N,N<sup>1</sup> - diphenyl urea, 7 parts of a non-ionogenic washing agent (obtained by condensing 2,4-diamyl phenol with 10-12 mols of ethylene oxide), 30 parts of sodium metasilicate and 58 parts of tetra-sodium pyrophosphate are well mixed together whereupon a cleansing agent having antibacterial properties is obtained. A 1% aqueous solution of this agent is excellently suitable as a disinfectant washing liquor for the cleansing of 110 clothes, crockery and other objects.

#### EXAMPLE 10

A disinfectant dry cleaning agent is obtained by dissolving 0.5 parts of 3,5,3<sup>1</sup>,5<sup>1</sup> - tetra - (trifluoromethyl) - N,N<sup>1</sup> - diphenyl urea and 5 parts of a condensation product of nonyl phenol with 15 mols of ethylene oxide in 94.5 parts of tetrachloroethane or the same amount 125 of trichloroethylene.

80

85

90

95

100

105

110

115

120

125

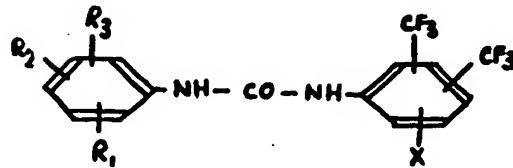
130

## EXAMPLE 11

An antibacterial skin cream is obtained by thoroughly mixing the following components: 5 13 parts of glycol monostearate, 1 part of sodium dodecyl sulphate, 2 parts of polyethylene glycol 1500, 3 parts of wax, 3 parts of viscous paraffin oil, 2 parts of wool fat, 3 parts of polyoxyethylene sorbitan mono-oleate, 10 6 parts of glycerine, 0.1 parts of perfume, 0.1 parts of p-hydroxybenzoic acid methylester, 2 parts of 3,5 bis - (trifluoromethyl) - 3<sup>1</sup>,4<sup>1</sup> - dichloro - N,N<sup>1</sup> - diphenyl urea. Instead of 3,5 bis - (trifluoromethyl) - 3<sup>1</sup>,4<sup>1</sup> - dichloro - N,N<sup>1</sup> - diphenyl urea, also 3,5 - bis - (trifluoromethyl) - 4<sup>1</sup> - chlorodiphenyl urea can be used.

## WHAT WE CLAIM IS:—

1. Process for the production of insecticidally and bactericidally active derivatives of 20 diphenyl urea of the general formula



I

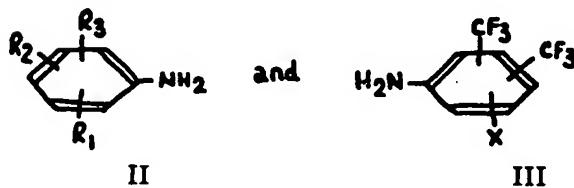
wherein R<sub>1</sub> represents hydrogen, a halogen atom, the trifluoromethyl group or the nitro group,

25 R<sub>2</sub> represents hydrogen, a halogen atom, the trifluoromethyl group or an alkyl or alkoxy radical having from 1 to 5 carbon atoms,

30 R<sub>3</sub> represents hydrogen, a halogen atom or a phenoxy or phenylmercapto radical possibly substituted by one or more chlorine atoms or alkyl groups having from 1 to 5 carbon atoms,

35 X represents hydrogen, a halogen atom or an alkoxy group having from 1 to 5 carbon atoms, which comprises reacting by known methods, possibly in steps and in any order desired, one

40 mol of a reactive derivative of carbonic acid with one mol of each of two aminobenzene compounds of the general formulae



II

III

wherein R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, and X have the meanings given above.

45 2. Process according to claim 1 for the production of 3,5 - bis - (trifluoromethyl) - di-

phenyl urea derivatives, which comprises using a 3,5 - bis - (trifluoromethyl) - aniline possibly substituted by a halogen atom, as starting material of the general formula III.

50

3. Process according to claim 1 for the production of symmetrically substituted diphenyl urea derivatives which comprises reacting 1 mol of a reactive derivative of carbonic acid, in particular phosgene, with 2 mols of a compound of the general formula III given in claim 1.

55

4. Process for the protection of keratin material from injurious insects, which comprises treating the material with agents which contain diphenyl urea derivatives of the general formula I given in claim 1.

60

5. Agents for the protection of keratin material from injurious insects, characterised by a content of diphenyl urea derivatives of the general formula I given in claim 1, such derivatives being in a finely distributed form, possibly combined with suitable carriers or solvents and/or distributing agents.

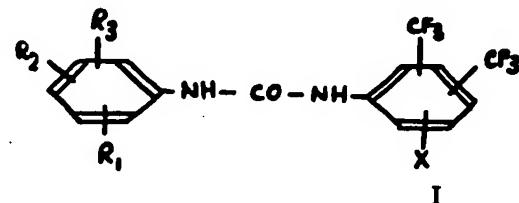
65

6. The keratin material protected from injurious insects by the use of compounds of the general formula I.

70

7. Diphenyl urea derivatives of the general formula

75



I

wherein R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and X have the meanings given in claim 1.

80

8. The manufacture of a disinfectant and disinfectant cleansing agent wherein at least one bacterial diphenyl urea derivative of the general formula I given in claim 1 is mixed with a capillary active agent.

85

9. A disinfectant and disinfectant cleansing agent comprising as active ingredients at least one bactericidal diphenyl urea derivative of the general formula I given in claim 1 and a capillary active agent, especially a cleansing agent.

90

10. A disinfectant and disinfectant cleansing agent according to claim 9 wherein the active ingredient is 3,5 - bis - (trifluoromethyl) - 3<sup>1</sup>,4<sup>1</sup> - dichloro - N,N<sup>1</sup> - diphenyl urea.

95

11. A disinfectant and disinfectant cleansing agent according to claim 9 wherein the active ingredient is 3,5 - bis - (trifluoromethyl) - 4<sup>1</sup> - chloro - N,N<sup>1</sup> - diphenyl urea.

95

12. A disinfectant and disinfectant cleansing agent according to claim 9 wherein the capillary active agent is an alkali metal soap of fatty acids having from 10 to 20 carbon atoms.

100

13. A process for the disinfection of in-  
organic and organic inanimate objects, in par-  
ticular of cellulosic fabrics, which comprises  
5 applying to them a disinfectant and disinfect-  
ant cleansing agent according to claim 9 with  
a content of at least one diphenyl urea deriva-  
tive of the general formula I as active in-  
gredient.

14. A process as claimed in claim 1 in  
10 which R<sub>3</sub> represents hydrogen, a halogen atom,  
or a phenoxy radical possibly substituted by  
one or more chlorine atoms.

15. Diphenyl urea derivatives as claimed in  
15 claim 7 in which R<sub>3</sub> represents hydrogen, a  
halogen atom, or a phenoxy radical possibly  
substituted by one or more chlorine atoms.

16. A process as claimed in claim 1 sub-  
stantially as hereinbefore described in any one  
of Examples 1 to 4. 20

17. A process as claimed in claim 14 sub-  
stantially as hereinbefore described in any one  
of Examples 1 to 4.

18. Diphenyl urea derivatives as claimed in  
claim 7 substantially as hereinbefore described  
in any one of the Examples. 25

19. Diphenyl urea derivatives as claimed  
in claim 15 substantially as hereinbefore des-  
cribed in any one of the Examples.

W. P. THOMPSON & CO.,  
12, Church, Street, Liverpool, 1.  
Chartered Patent Agents.

Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press  
(Leamington) Ltd.—1963. Published by The Patent Office, 25 Southampton Buildings,  
London, W.C.2, from which copies may be obtained.